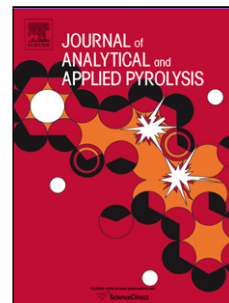


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Flash vacuum pyrolysis of benzylidene halides, benzotrihalides and aryl halides over magnesium

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Abstract

Flash vacuum pyrolysis at 600 °C through glass wool coated with freshly sublimed magnesium is examined as a preparative method for dehalogenative coupling in organic synthesis. Substituted benzyldene chlorides give predominantly the corresponding stilbenes and in some cases these are readily isolated in pure form. With an *ortho*-halogen substituent, additional cyclisation gives phenanthrenes but the method is not compatible with the presence of several reactive groups. An *ortho*-methoxy substituent leads to unexpected formation of mono- and dimethyl products. With 1,4-bis(dihalomethyl)benzenes, halogenated polymers are deposited directly from the gas phase via generation of halogenated *p*-xylylenes. The 1,2- and 1,3-isomers lead respectively to benzocyclobutadiene, isolated as a dimer, and to pyrene. The 1,4-bis(trihalomethyl)benzenes give more highly halogenated polymers directly from the gas phase via halogenated *p*-xylylenes. While halobenzenes generally give the corresponding benzenes and biphenyls, 1,2-dihalobenzenes additionally produce triphenylene in preparatively useful yield by a process not involving intermediacy of free benzyne.

Keywords: Flash vacuum pyrolysis; Dehalogenation; Coupling; Polymers

1 Introduction

Some time ago we described the application of flash vacuum pyrolysis (FVP) over a layer of freshly sublimed magnesium on glass wool as a preparatively useful method for dehalogenative coupling of benzyl halides, and the effect of these conditions on a wide range of haloalkanes, -alkenes and -alkynes was also examined [1,2]. The same method was later used in dehalogenation of dichlorophosphines to generate simple alkylphosphinidenes [3] and an arylphosphinidene [4]. More recently the occurrence of an unusual rearrangement during such dehalogenative coupling of halogenated methylthiophenes to form benzodithiophenes was also described [5]. In this paper, the further application of these inherently clean, solvent-free conditions to dehalogenative coupling of benzylidene chlorides, benzotrihalides and aryl halides is reported.

2 Experimental

2.1 General

Melting points were recorded on a Kofler hot-stage microscope and are uncorrected. Infra red spectra were recorded as Nujol mulls for solids and as thin films for liquids on a Perkin Elmer 1420 instrument. NMR spectra were obtained for ^1H at 80 MHz using a Bruker WP80 instrument or at 300 MHz using a Bruker AM300 instrument, for ^{13}C at 75 MHz using a Bruker AM300 instrument and for ^{19}F at 75 MHz using a Bruker WP80 instrument. All spectra were run on solutions in CDCl_3 with internal Me_4Si as reference for ^1H and ^{13}C and CFCl_3 for ^{19}F . Chemical shifts are reported in ppm to high frequency of the reference and coupling constants J are in Hz. Solid state CP-MAS ^{13}C NMR spectra were obtained at 125 MHz on a Bruker MSL 500 spectrometer. Mass spectra were obtained on an A. E. I. MS-902 spectrometer using electron impact at 70 eV. GCMS was carried out using a Hewlett Packard 5890A coupled to a Finnigan-Incos 50 mass spectrometer. Thermogravimetric analysis was conducted using a Perkin Elmer Series 7 thermal analysis system over the temperature range 30–900 °C.

2.2 Preparation of Substituted Benzylidene Chlorides

These were prepared from the corresponding benzaldehydes either by reaction with 1 equivalent of thionyl chloride heated under reflux in the absence of solvent for 2 h (Method A), reaction with 1 equivalent of thionyl chloride in CH_2Cl_2 heated under reflux for 2 h (Method B), reaction with 1 equivalent of PCl_5 in CH_2Cl_2 at room temperature for 2 h (Method C), or reaction with 1 equivalent of PCl_5 in CH_2Cl_2 heated under reflux for 2 h (Method D). Work up by addition to water, extraction with ether, drying and evaporation (Method A), evaporation (Method B), or washing with water, drying and evaporation (Methods C and D) was then followed in each case by kugelrohr distillation to give the product as follows:

2.2.1 Benzylidene chloride 1a. Prepared from benzaldehyde (Method A, 87%) as a colourless liquid, bp 85 °C at 10 Torr (lit. [6] 89–90 °C at 10 Torr); δ_{H} 6.80 (1 H, s) and 7.3–7.7 (5 H, m).

2.2.2 2-Methylbenzylidene chloride 1b. Prepared from *o*-tolualdehyde (Method A, 86%) as a colourless liquid, bp 60 °C at 1.0 Torr (lit. [7] 105–107 °C at 16 Torr); δ_{H} 2.40 (3 H, s), 7.00 (1 H, s), 7.2–7.4 (3 H, m) and 7.8–8.0 (1 H, m).

2.2.3 3-Methylbenzylidene chloride 1c. Prepared from *m*-tolualdehyde (Method B, 89%) as a colourless liquid, bp 130 °C at 20 Torr (lit. [7] 110–111 °C at 15 Torr); δ_{H} 2.30 (3 H, s), 6.60 (1 H, s) and 7.0–7.4 (4 H, m).

2.2.4 4-Methylbenzylidene chloride 1d. Prepared from *p*-tolualdehyde (Method B, 71%) as a colourless crystalline solid, bp 130 °C at 20 Torr; mp 45–47 °C (lit. [8] 47 °C); δ_{H} 2.40 (3 H, s), 6.80 (1 H, s), 7.30 and 7.60 (4 H, AB pattern, *J* 8).

2.2.5 2-Methoxybenzylidene chloride 1e. Prepared from *o*-anisaldehyde (Method C, 91%) as a colourless liquid, bp 100 °C at 1.0 Torr (lit. [9] 231 °C); δ_{H} 3.70 (3 H, s), 6.70 (1 H, m), 6.93 (1 H, m), 7.18 (1 H, s), 7.23 (1 H, m), and 7.80 (1 H, m); δ_{C} 55.5 (OMe), 66.5 (CHCl₂), 110.7 (C-3), 121.0, 127.9, 128.4 (C-1), 131.2 and 154.3 (C-2).

2.2.6 1-Dichloromethyl-2-methoxynaphthalene 10. Prepared from 2-methoxy-1-naphthaldehyde (Method D, 69%) as a colourless solid, mp 124–125 °C (lit. [10] 125–127 °C); δ_{H} 3.92 (3 H, s), 7.12 (1 H, d), 7.40 (1 H, t), 7.60 (1 H, t), 7.70–7.85 (2 H, m), 7.87 (1 H, s, CHCl₂) and 8.75 (1 H, m, 8-H) (lit. [10] 3.93 (s), 7.14 (d), 7.3–7.83 (m), 7.90 (s) and 8.26 (dd)); δ_{C} 56.7 (OMe), 64.6 (CHCl₂), 112.2 (C-3), 124.1, 125.0, 126.9, 128.8, 129.7 (4ry), 130.6 (4ry), 132.8, 137.6 (4ry) and 152.3 (C-2).

2.2.7 4-Methoxybenzylidene chloride 1f. Prepared from *p*-anisaldehyde (Method B, 77%), as a colourless liquid, bp 100 °C at 1.0 Torr (lit. [11] 130–132 °C at 14 Torr); δ_{H} 3.73 (3 H, s), 6.63 (1 H, s), 6.85 and 7.45 (4 H, AB pattern, *J* 9).

2.2.8 2-Chlorobenzylidene chloride 1g. Prepared from 2-chlorobenzaldehyde (Method D, 85%) as a colourless liquid, bp 120 °C at 1.0 Torr (lit. [7] 226–228 °C); δ_{H} 7.00 (1 H, s), 7.0–7.3 (3 H, m) and 7.6–7.8 (1 H, m).

2.2.9 4-Chlorobenzylidene chloride 1h. Prepared from 4-chlorobenzaldehyde (Method D, 77%) as a colourless liquid, bp 120 °C at 1.0 Torr (lit. [7] 236 °C); δ_{H} 6.70 (1 H, s) and 7.35 and 7.54 (4 H, AB pattern, *J* 9).

2.2.10 2-Chloro-6-fluorobenzylidene chloride 1i. Prepared from 2-chloro-6-fluorobenzaldehyde (Method C, 86%) as a colourless liquid, bp 100 °C at 1.0 Torr (lit. [12] 95 °C at 16 Torr); δ_{H} 6.9–7.4 (3 H, m) and 7.20 (1 H, s).

2.2.11 6-Chloro-3,4-methylenedioxybenzylidene chloride 1j. Prepared from 6-chloro-3,4-methylenedioxybenzaldehyde (Method D, 93%) as colourless crystals, mp 43–44 °C (Found: C, 40.3; H, 1.9. C₈H₅Cl₃O₂ requires C, 40.1; H, 2.1%); δ_{H} 6.09 (2 H, s), 6.85 (1 H, s), 7.19 (1 H, s) and 7.45 (1 H, s); δ_{C} 68.2 (CHCl₂), 102.4, 108.0, 109.0, 123.2 (4ry), 130.9 (4ry), 147.5 (4ry) and 149.4 (4ry); *m/z* 238 (³⁵Cl₃-M⁺, 50%), 203 (100), 173 (5), 147 (18), 133 (8), 111 (28), and 74 (33).

2.2.12 2-Chloro-5-nitrobenzylidene chloride 1k. Prepared from 2-chloro-5-nitrobenzaldehyde (Method D, 90%) as colourless crystals, mp 31–32 °C (Found: C, 35.4; H, 1.6; N, 5.6. C₇H₄Cl₃NO₂ requires C, 35.0; H, 1.7; N, 5.8%); δ_{H} 7.25 (1 H, s), 7.71 (1 H, d, *J* 9), 8.34 (1 H, d of d, *J* 9, 3) and 8.94 (1 H, d, *J* 3); δ_{C} 66.6 (CHCl₂), 124.2, 125.5, 130.9, 137.5 (4ry), 139.3 (4ry) and 147.2 (4ry); *m/z* 239 (³⁵Cl₃-M⁺, 35%), 204 (100), 158 (50), 123 (96), 97 (40) and 73 (70).

2.2.13 2-Bromo-4,5-dimethylbenzylidene chloride **1l**.

2-Bromo-4,5-dimethylbenzaldehyde was first prepared by reaction of 4,5-dibromo-*o*-xylene [13] (see section 2.7.1) with butyllithium followed by DMF at $-70\text{ }^{\circ}\text{C}$ (50%) to give a pale yellow solid, mp $64\text{--}65\text{ }^{\circ}\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 3050, 1690, 1595, 1250, 1180, 1140, 1035, 975, 915, and 865; δ_{H} 2.30 (3 H, s), 2.33 (3 H, s), 7.54 (1 H, s), 7.80 (1 H, s) and 10.43 (1 H, s); δ_{C} 19.1, 19.9, 124.1 (4ry), 130.3, 131.1 (4ry), 134.4, 136.8 (4ry), 145.7 (4ry) and 191.5; m/z 214/212 (M^+ , 59, 66%), 213/211 (95, 100), 185 (16), 132 (11), 103 (61) and 77 (64).

The title compound was then prepared using this aldehyde (Method B, 75%) as a colourless liquid, bp $100\text{ }^{\circ}\text{C}$ at 5.0×10^{-2} Torr (Found: C, 40.6; H, 3.2. $\text{C}_9\text{H}_9\text{BrCl}_2$ requires C, 40.3, H, 3.4%); δ_{H} 2.30 (3 H, s), 2.37 (3 H, s), 7.25 (1 H, s), 7.45 (1 H, s), and 7.85 (1 H, s); δ_{C} 19.3, 19.4, 70.7 (CHCl_2), 117.2 (4ry), 129.7 133.1, 136.3, (4ry) 137.3, (4ry) and 140.7 (4ry); m/z 270/268/266 (M^+ , 4, 10, 6%), 233/231 (100, 85), 152 (8), 115 (57), 89 (14) and 75 (17).

2.3 Pyrolysis of Substituted Benzylidene Chlorides over Magnesium.

The procedure used was based on that reported previously [1,2]. Using the standard apparatus for FVP [14], the required weight of magnesium turnings was placed at the centre of the furnace tube which was loosely packed with glass wool. The system was connected up to the vacuum pump with a stopper in place of the sample inlet, placed under vacuum, and heated to $700\text{ }^{\circ}\text{C}$ resulting in the metal melting and subliming over the glass wool. The system was then isolated from the pump, cautiously refilled with nitrogen and after allowing the furnace to cool to the operating temperature (600 or $650\text{ }^{\circ}\text{C}$), the sample inlet tube was attached and the pyrolysis conducted as normal. The products in the cold trap were dissolved out while still cold using CDCl_3 and analysed using NMR and GCMS. Yields were determined by adding a known weight of an internal standard to the solution for ^1H NMR and comparing integrals and/or calibration of GC signals.

Pyrolysis of benzylidene chlorides **1a–j** was carried out as described above, typically on a 0.5–1.0 g scale, and the results are given in Table 1. In most cases the major product was the corresponding (*E*)-stilbene **2** and this was obtained in some cases in pure form by recrystallisation of the crude solid product from the furnace exit using EtOH. Physical and spectroscopic data for the most significant products are as follows:

2.3.1 From FVP of **1a**

(*E*)-stilbene **2a**, mp $120\text{--}122\text{ }^{\circ}\text{C}$ (lit. [15] $124\text{ }^{\circ}\text{C}$); δ_{H} 7.10 (2 H, s), 7.2–7.35 (6 H, m) and 7.50 (4 H, m); δ_{C} 126.4 (C-2, C-6), 127.5 (C-4), 128.5 (C-3, C-5, C- α), and 137.2 (C-1).

2.3.2 From FVP of **1b**

benzocyclobutene **9**, δ_{H} 3.02 (4 H, s) and 6.9–7.2 (4 H, s); m/z 104;
(*E*)-2,2'-dimethylstilbene **2b**, δ_{H} 2.45 (6 H, s) and 7.1–7.5 (10 H, m); m/z 208;
2,2'-dimethylbibenzyl **4b**, δ_{H} 2.38 (6 H, s), 2.88 (4 H, s) and 7.1–7.5 (8 H, m); m/z 210.

2.3.3 From FVP of **1c**

(*E*)-3,3'-dimethylstilbene **2c**, δ_{H} 2.40 (6 H, s), 7.12 (2 H, s) and 7.1–7.4 (8 H, m); δ_{C} 21.4 (Me), 123.7 (C-6), 127.2 (C-2), 128.3 (C-4), 128.5 and 128.6 (C-5 and C- α), 137.4 (C-1) and 138.1 (C-3); m/z 208;

3,3'-dimethylbibenzyl **4c**, δ_{H} 2.36 (6 H, s), 2.90 (4 H, s), and 7.1–7.4 (8 H, m); δ_{C} 21.4 (Me), 38.0 (CH₂), 125.4 (C-6), 126.6 (C-4), 128.2 (C-5), 129.2 (C-2), 137.8 (C-3) and 141.9 (C-1); m/z 210.

2.3.4 From FVP of **1d**

(*E*)-4,4'-dimethylstilbene **2d**, mp 183–184 °C (lit. [16] 181.7 °C); δ_{H} 2.35 (6 H, s), 7.02 (2 H, s), 7.15 and 7.40 (8 H, AB pattern, *J* 9); δ_{C} 21.2 (Me), 126.3 (C-2), 127.6 (C- α), 129.3 (C-3), 134.7 (C-1) and 137.2 (C-4); m/z 208;

4,4'-dimethylbibenzyl **4d**, δ_{H} 2.5 (6 H, s), 3.0 (4 H, s) and 7.2–7.6 (8 H, m); m/z 210.

2.3.5 From FVP of **1f**

p-methoxystyrene, δ_{H} 3.75 (3 H, s), 5.12 (1 H, d of d, *J* 10, 2), 5.60 (1 H, d of d, *J* 18, 2), 6.64 (1 H, d of d, *J* 18, 10) and 7.0–7.4 (4 H, m); m/z 134.

2.3.6 From FVP of **1h**

(*E*)-4,4'-dichlorostilbene **2h**, mp 177–178 °C (lit. [17] 176 °C); δ_{H} 7.17 (2 H, s) and 7.47 and 7.57 (8 H, AB pattern, *J* 9); δ_{C} 127.7 (C-2), 128.0 (C- α), 128.9 (C-3), 133.5 (C-4) and 135.5 (C-1).

2.3.7 From FVP of **1i**

Preparative TLC using petroleum ether as solvent gave (*E*)-2,2'-dichloro-6,6'-difluorostilbene **2i** as colourless crystals, mp 106–107 °C (Found: C, 58.8; H, 2.3. C₁₄H₈Cl₂F₂ requires C, 58.9; H, 2.8%); $\nu_{\text{max}}/\text{cm}^{-1}$ 3080, 1720, 1605, 1575, 1250, 1215, 1160, 980, 900, 780 and 730; δ_{H} 7.0–7.3 (6 H, m) and 7.5 (2 H, s); δ_{C} 114.8 (C-5, d, *J* 23), 124.2 (C-1, d, *J* 14), 125.7 (C-3, d, *J* 3), 126.8 (C-4, d, *J* 13), 128.7 (C- α , d, *J* 10), 134.8 (C-2, d, *J* 5) and 161.1 (C-6, d, *J* 253); m/z 284 (M⁺, 28%), 248 (5), 214 (100), 194 (15), 154 (8), 124 (24) and 106 (42); δ_{F} –83.6.

(*Z*)-2,2'-dichloro-6,6'-difluorostilbene **3i**, δ_{C} 113.8 (C-5, d, *J* 21), 114.3 (C-1, d, *J* 22), 125.0 (C-3, d, *J* 3), 126.6 (C-4, d, *J* 18), 130.2 (C- α , d, *J* 10), 130.8 (C-2, d, *J* 9) and 163.2 (C-6, d, *J* 255); m/z 284 (M⁺, 35%), 249 (5), 214 (100), 194 (23), 154 (12), 124 (20) and 106 (45).

2.3.8 FVP of 1-Dichloromethyl-2-methoxynaphthalene **10**

FVP of the title compound (0.53 g, 600 °C, 5.0×10^{-1} Torr, inlet 85–90 °C, 1.5 g magnesium) gave a liquid product which was shown by NMR and GCMS to consist of 1-methylnaphthalene (51%); δ_{H} 2.63 (3 H, s), 7.3–8.1 (7 H, m); δ_{C} 19.3 (CH₃), 124.1 (C-8), 125.5 (C-7), 125.7 (C-3), 125.8 (C-6), 126.3 (C-4), 127.8 (C-5), 128.5 (C-2), 132.6 (C-9), 133.5 (C-10) and 134.2 (C-1); m/z 142;

1,2-dimethylnaphthalene (10%); δ_{H} 2.40 (3 H, s), 2.50 (3 H, s) and 7.3–8.1 (6 H, m); δ_{C} 14.5 (1-CH₃), 21.0 (2-CH₃); m/z 156 and small amounts of ethylnaphthalene; m/z 156, and 2-methylnaphthalene.

2.4 Preparation and FVP of tetrahaloxylenes

2.4.1 Preparation of $\alpha,\alpha,\alpha',\alpha'$ -tetrachloro-*p*-xylene **11**

This was prepared from terephthalaldehyde (5.0 g, 37.3 mmol) and phosphorus pentachloride (16.0 g, 77.0 mmol) in dichloromethane, stirred at room temperature for

2 h. Excess PCl_5 was destroyed by adding water and the organic layer dried and evaporated to give a crystalline solid which was recrystallised from petroleum ether to give $\alpha,\alpha,\alpha',\alpha'$ -tetrachloro-*p*-xylene (8.1 g, 90%) as colourless crystals, mp 93–95 °C (lit. [18] 92–94 °C); δ_{H} 6.7 (2 H, s) and 7.6 (4 H, s); m/z 244.

2.4.2 Preparation of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylene **12**

This was prepared from terephthalaldehyde (2.0 g, 14.9 mmol) and thionyl bromide (6.2 g, 29.8 mmol) [19] heated under reflux at 100–120 °C for 3 h. On cooling, the residual acidic fumes were removed with a stream of N_2 gas and the solid residue taken up in hot chloroform. Cooling on an ice-bath gave fine solid precipitate of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylene (3.8 g, 61%), mp 169–170 °C (lit. [20] 169 °C); δ_{H} (CD_3COCD_3) 7.2 (2 H, s) and 7.7 (4 H, s); m/z 422.

□□□□□ □□□□□□ $\alpha,\alpha,\alpha',\alpha'$ -tetrachloro-*p*-xylene **11**

FVP of the title compound (2.2 g, 600 °C, 8.0×10^{-1} Torr, inlet 95–100 °C, 2.0 g magnesium) gave as main product a polymeric material coated in the cold trap, with a trace of a liquid which consisted of *p*-xylene (1%), toluene (0.6%) and benzene (0.8%). As the polymer was insoluble in conventional solvents, it was simply peeled off from the cold trap. Microanalysis of the material was indicative of *poly*(α,α' -dichloro-*p*-xylylene) **14** (Found: C, 59.6; H, 3.4. $(\text{C}_8\text{H}_6\text{Cl}_2)_n$ requires C, 55.5; H, 3.5%) and the yield of the polymer was 77% (1.20 g); δ_{C} (solid state) 66.7 (CHCl), 128.3 (4 aromatic C) and 140.1 (2 quaternary aromatic C). Thermal analysis showed that the material started degrading at a temperature as low as 50 °C in both an N_2 and air atmosphere but it finally decomposed at about 400 °C under N_2 and 600 °C in air. The material gave a sharp isotherm at about 50 °C in both air and N_2 .

□□□□□ □□□□□□ $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylene **12**

FVP of the title compound (0.98 g, 600 °C, 1.5×10^{-2} Torr, inlet 150–160 °C, 2.0 g magnesium) gave a faint yellow polymeric material as the only product, which was worked up as above. Microanalysis of the material was indicative of *poly*(α,α' -dibromo-*p*-xylylene) **15** (Found: C, 40.9; H, 2.0. $(\text{C}_8\text{H}_6\text{Br}_2)_n$ requires C, 36.7; H, 2.3%) and the yield of polymer was 25% (0.15 g); δ_{C} (solid state) 62.3 (CHBr), 128.9 (4 aromatic CH) and 139.9 (2 quaternary aromatic C). Thermal analysis on the material showed that it was stable in an N_2 or air atmosphere up to 200 °C after which there was a gradual weight loss up to 500 °C at which point it decomposed.

□□□□□ □□□□□□ $\alpha,\alpha,\alpha',\alpha'$ -tetrachloro-*o*-xylene **16**

FVP of the title compound (1.1 g, 600 °C, 8.0×10^{-2} Torr, inlet 85–90 °C, 1.5 g magnesium) gave a faint yellow liquid and a solid. The NMR and GCMS showed that the two fractions consisted of the same mixture of compounds namely:

7,8-dichlorobicyclo[4.2.0]octa-1,3,5-triene [21] (*cis* and *trans*, 50%), *cis*-isomer; δ_{H} 5.6 (2 H, s) and 7.3 (4 H, m); δ_{C} 68.1 (C-7, C-8), 123.0 (C-2, C-5), 131.0 (C-3, C-4) and 138.2 (C-1, C-6), *trans*-isomer; δ_{H} 5.2 (2 H, s) and 7.3 (4 H, m); δ_{C} 62.2 (C-7, C-8), 122.9 (C-2, C-5), 131.3 (C-3, C-4) and 141.3 (C-1, C-6); m/z 173 and *7,7,8-trichlorobicyclo[4.2.0]octa-1,3,5-triene* [22] (18%); δ_{H} 5.7 (1 H, s) and 7.2–7.5 (4 H, m); δ_{C} 60.7, 71.2, 128.2, 128.5, 130.4, 132.0, 143.1, and 145.8; m/z 208. There were also small amounts of 7-chlorobicyclo[4.2.0]octa-1,3,5-triene and bicyclo[4.2.0]octa-1,3,5-triene.

Repeat pyrolysis at higher magnesium to substrate ratio (1.0 g of **16**, 600 °C, 1.2×10^{-2} Torr, inlet 85–90 °C, 2.8 g magnesium) gave only a yellow solid product which consisted of 7,8-dichloro-bicyclo[4.2.0]octa-1,3,5-triene (15%) and benzocyclobutadiene dimer [23] **18** (45%); δ_{C} 43.2, 43.7, 120.7, 121.5, 125.9, 126.7, 126.8, 127.6 (3C), 127.7 (2C), 133.1, 134.7, 148.5 and 149.0; m/z 204, with only trace amounts of the trichlorobicyclo[4.2.0]octa-1,3,5-triene. The yields were determined from the GC integral.

□□□□□ □□□□□ $\alpha,\alpha,\alpha',\alpha'$ -tetrachloro-*m*-xylene **19**

FVP of the title compound (0.96 g, 600 °C, 4.2×10^{-2} Torr, inlet 150–160 °C, 1.7 g magnesium) showed only two products: *pyrene* (54%); δ_{H} 8.1–8.2 (m); δ_{C} 124.9 (6 C, C-1, C-10b), 125.8 (2 C, C-2), 127.4 (4 C, C-4) and 131.1 (4 C, C-3a); m/z 202, and 3,3'-dimethylstilbene (5%).

2.5 FVP of dichlorodiphenylmethane **22**

FVP of the title compound (1.50 g, 600 °C, 1.0×10^{-1} Torr, inlet 50 °C, 1.54 g magnesium) gave a solid product which was shown by GCMS to contain *diphenylmethane* (7%); m/z 168, 1,1-diphenylethene (1%); m/z 180, *fluorene* (25%); m/z 166, triphenylmethane (2%); m/z 244, 1,1,1-triphenylethane (1%); m/z 258, *tetraphenylethene* (39%); m/z 332, 1,1,2,2-tetraphenylethane (1%); m/z 167 ($M^+/2$), and 9-(diphenylmethylene)*fluorene* **23** (5%); m/z 330.

2.6 FVP of mono- and bis(trihalomethyl)benzenes

2.6.1 FVP of benzotrichloride **24**

FVP of the title compound (0.43 g, 600 °C, 2.0×10^{-1} Torr, inlet room temperature, 0.8 g magnesium) gave mainly a yellow solid with a trace of liquid. The liquid fraction was mainly traces of benzylidene chloride and starting material. The NMR and GCMS of the solid fraction showed that it consisted of $\alpha,\alpha,\alpha',\alpha'$ -tetrachlorobibenzyl **25** (22%); δ_{C} 126.6 (4 C), 128.2 (4 C), 129.0, 129.1 and 137.5; m/z 320, (*E*)- α,α' -dichlorostilbene **26** (23%); m/z 249, (*Z*)- α,α' -dichlorostilbene **27** (19%); m/z 249, and *diphenylacetylene* **28** (12%); m/z 178.

Repeat pyrolysis at longer contact time (1 Torr) gave a yellow solid, which consisted of $\alpha,\alpha,\alpha',\alpha'$ -tetrachlorobibenzyl **25** (8%), (*E*)- and (*Z*)- α,α' -dichlorostilbene **26** and **27** (21% and 20%); δ_{C} 128.2 (4 C), 129.0, 129.1 (4 C), 130.7 and 137.5 for one isomer and δ_{C} 128.2 (4 C), 128.5, 129.7 (4 C), 129.8 and 137.1 for the other, and *diphenylacetylene* **28** (30%); δ_{C} 89.4, 123.2, 128.1 (4 C), 128.3 and 131.6 (4 C). The yields were determined from GC integration.

2.6.2 FVP of benzotrifluoride

FVP of the title compound (0.39 g, 600 °C, 40 Torr (N_2 leak), inlet ice-cooled vertical inlet tube, 0.5 g magnesium) gave mainly a liquid fraction, with a small amount of solid. The GCMS indicated the liquid fraction was mainly recovered starting material. While the solid contained various fluorinated compounds, the major ones were $\alpha,\alpha,\alpha',\alpha'$ -tetrafluorobibenzyl; m/z 254, bis(trifluoromethyl)biphenyl; m/z 290, α,α' -difluorostilbene; m/z 216, α -fluorostilbene; m/z 198, fluorophenanthrene; m/z 196, *diphenylacetylene*; m/z 178, α,α,α' -trifluorobibenzyl; m/z 236, and small amounts of various unidentified compounds. Product identification was based entirely on GCMS evidence and no attempt was made to determine the yield of the products, as most of the starting material was unreacted.

2.6.3 FVP of 1,4-bis(trichloromethyl)benzene **29**

FVP of the title compound (1.54 g, 600 °C, 4.4×10^{-2} Torr, inlet 130–135 °C, 2.0 g magnesium) gave a white polymer, which was insoluble in conventional solvents. Microanalysis of the polymer was consistent with expectation for *poly*($\alpha,\alpha,\alpha',\alpha'$ -tetrachloro-*p*-xylylene) **32** (Found: C, 38.6; H, 1.2. $(C_8H_4Cl_4)_n$ requires C, 39.7; H, 1.7%) and the yield of the polymer was 94% (1.16 g); δ_C (solid state) 97.8 (2CCl₂), 131.7 (C-2, C-3, C-5, C-6) and 140.4 (C-1, C-4). Using CHCl₂ end group analysis, the polymer was estimated to consist of 10 units, giving an approximate molecular weight of 2420. Thermal analysis of the polymer in air showed a double isotherm at 300 °C and 390 °C; and a gradual weight loss was observed from 300 °C to 540 °C. In an N₂ atmosphere, a single isotherm was observed at 360 °C, after which a gradual weight loss continued up to 650 °C.

2.6.4 FVP of 1,4-bis(trifluoromethyl)benzene **30**

FVP of the title compound (1.49 g, 600 °C, 2.0 Torr, inlet ice-cooled vertical inlet tube, 1.5 g magnesium) gave two fractions, a white polymer and a liquid, as product. The ¹H NMR and GCMS data showed that the liquid consisted mainly of the starting material and numerous fluorinated compounds. The polymer was insoluble in conventional solvents. Microanalysis of the material was indicative of *poly*($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) **33** (Found: C, 54.6; H, 2.2. $(C_8H_4F_4)_n$ requires C, 54.6; H, 2.3%) and the yield of polymer was 33% (0.40 g). Solid state ¹³C NMR of the material was not obtained, because the material was electrostatic and therefore could not be obtained in a form suitable for measurement. Thermogravimetric analysis indicated that the polymer was stable up to 620 °C in nitrogen and 570 °C in air; there was however a gradual weight loss of about 25% between 50 and 500 °C in both air and nitrogen.

2.6.5 FVP of *p*-(bromomethyl)benzotrifluoride **34**

FVP of the title compound (0.81 g, 600 °C, 8.0×10^{-2} Torr, inlet room temperature, 1.2 g magnesium) gave a solid and a polymeric material as products. The ¹H NMR and GCMS of the solid showed that it was mainly recovered starting material (30%), with a small amount of 4,4'-bis(trifluoromethyl)bibenzyl (4%); δ_H 2.9 (4 H, s) and 7.1–7.4 (8 H, m); *m/z* 318, 4-trifluoromethyltoluene (8%); δ_H 2.3 (3 H, s) and 7.1–7.4 (4 H, m); *m/z* 160, and α -bromo- α',α' -difluoro-*p*-xylene (trace); *m/z* 219.

Microanalysis of the polymer was indicative of *poly*(α,α -difluoro-*p*-xylylene) **36** (Found: C, 64.1; H, 4.3; $C_8H_6F_2$ requires C, 68.6; H, 4.3%) and the yield of the polymer was 12.6% (42.1 mg); δ_C (solid state) 36.8 (CH₂, br), 79.3 (CF₂, br), 120.2 (C-2, C-3, C-5, C-6, br) and 160.7 (C-1, C-4, br). Based on end group analysis (CH₃, δ_C 13.0) it was estimated to have a molecular weight of 990 (*i.e.* a heptamer). Thermogravimetric analysis of the polymer showed that it was stable in air up to 500 °C but underwent a steady weight loss from about 100 °C. Similar analysis in N₂ showed double isotherms at 100 °C and 550 °C, but it also underwent a steady weight loss from about 100 °C.

2.7 Preparation and FVP of halobenzenes

2.7.1 Preparation of 3,4-dibromo-*o*-xylene **42** [24]

This was prepared from 5-bromo-4-amino-*o*-xylene [25] (10.0 g, 50 mmol) which was dissolved in 48% hydrobromic acid (80 cm³) and water (300 cm³) at –5 to +5 °C

and the mixture was then diazotised with a 10% solution of sodium nitrite. The diazonium salt solution was slowly siphoned, under slight N₂ pressure, into a solution of cuprous bromide (100 g) in conc. hydrobromic acid (270 cm³) and H₂O (100 cm³) kept at 90 °C over a period of 30 min. After a further 30 min, the solution was allowed to cool, extracted with ether, dried and solvent evaporated to give a solid mass. Recrystallisation from ethanol gave *4,5-dibromo-o-xylene* (10.4 g, 79%) as light yellow plates, mp 88 °C (lit. [13] 88 °C); δ_{H} 2.2 (6 H, s) and 7.5 (2 H, s); δ_{C} 19.7, 121.7, 134.8 and 138.2.

2.7.2 FVP of chlorobenzene

FVP of chlorobenzene (0.63 g, 700 °C, 15 Torr (N₂ leak), 1.0 g magnesium) gave two fractions, a liquid and a solid. The liquid fraction was found to be *benzene* (60%); δ_{H} 7.25 (s); m/z 78, while the solid was *biphenyl* (28%); δ_{H} 7.3–7.5 (m); m/z 154. Both products were further confirmed by comparison with authentic samples by GC (OV101, 150 °C).

2.7.3 FVP of *o*-dichlorobenzene **37**

FVP of the title compound (1.38 g, 600 °C, 6.8×10^{-1} Torr, inlet room temperature, 2.0 g magnesium) gave three fractions, a liquid, a solid in the cold trap and a solid at the furnace exit. The NMR and GCMS indicated that the liquid product was mainly the starting material and *benzene* (13%), while the solid in the cold trap was mainly *biphenyl* (3%) with trace amounts of *biphenylene* **40**. The solid at the furnace exit consisted mainly of *triphenylene* **41** (6%) with small amounts of biphenyl and terphenyls.

Repeat pyrolysis at 700 °C under the same conditions gave a similar product mixture to above. The product mixture was kugelrohr distilled (100 °C at 20 Torr) leaving behind the solid product (0.11 g, 11%). The solid consisted of *triphenylene* **41** (80% composition); δ_{H} 7.65 (6 H, m) and 8.65 (6 H, m); δ_{C} 123.4 (6 C), 127.3 (6 C) and 129.9 (6 C); m/z 228, *biphenyl* (12% composition); δ_{H} 7.3–7.6 (m); δ_{C} 127.3 (6 C), 128.8 (4 C) and 141.2 (2 C); m/z 154, and *biphenylene* **40** (8% composition); δ_{H} 6.6 (4 H, m) and 6.7 (4 H, m); δ_{C} 117.4 (4 C), 128.3 (4 C) and 151.5 (4 C); m/z 152. All products were further confirmed with authentic samples by GC (OV101, 250 °C).

2.7.4 FVP of *o*-dibromobenzene **38**

FVP of the title compound (2.0 g, 600 °C, 8.0×10^{-1} Torr, inlet 60–65 °C, 2.0 g magnesium) gave a liquid and a solid product. The NMR and GCMS analysis indicated that the liquid product was mainly unreacted starting material with small amounts of benzene and bromobenzene. The solid fraction (73 mg, 11% corrected for recovered starting material) consisted mainly of *triphenylene* **41**; m/z 228, with small amounts of *biphenyl*; m/z 154 and *biphenylene* **40**; m/z 152.

Repeat pyrolysis at 700 °C under the same conditions gave a liquid and a solid product. The liquid product was only *benzene* (18%); δ_{H} 7.3 (s), while the solid product consisted of *triphenylene* **41** (13%), *biphenyl* (4%) and *biphenylene* **40** (1%). The ¹H and ¹³C NMR values for triphenylene, biphenyl and biphenylene, were the same as above and all products were further confirmed with authentic samples by GC (OV101, 250 °C).

2.7.5 FVP of *l*-bromo-2-chlorobenzene **39**

FVP of the title compound (1.07 g, 600 °C, 1.0×10^{-1} Torr, inlet room temperature, 1.5 g magnesium) gave three fractions, a liquid, a solid in cold trap and a solid at

furnace exit. The ^1H NMR indicated that the liquid product consisted of the starting material and benzene, while the solid in the cold trap consisted of biphenyl (6%); δ_{H} 7.35 (2 H, m), 7.45 (4 H, m) and 7.6 (4 H, m), and *biphenylene* **40** (1%); δ_{H} 6.65 (4 H, m) and 6.75 (4 H, m) with traces of benzene. The solid at the furnace exit was *triphenylene* **41** (11%); δ_{H} 7.65 (6 H, m) and 8.65 (6 H, m). All products were further confirmed with authentic samples by GC (OV101; 250°C).

2.7.6 FVP of 3,4-dibromo-*o*-xylene **42**

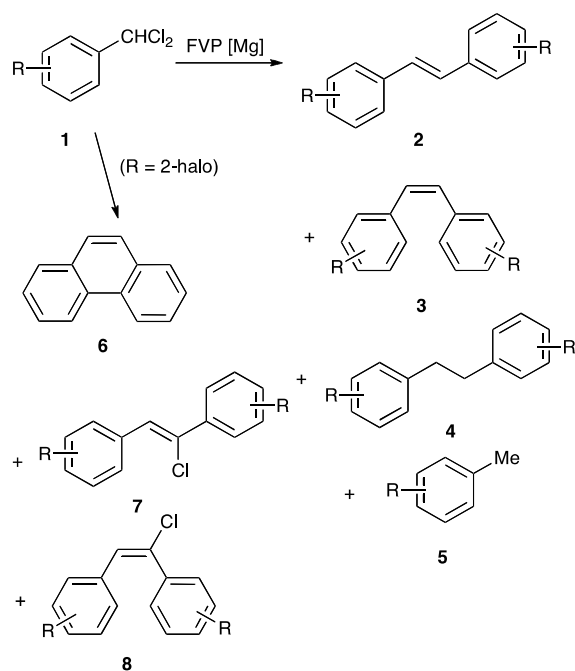
FVP of the title compound (1.12 g, 600 °C, 4.0×10^{-2} Torr, inlet 85–90 °C, 3.0 g magnesium) gave mainly a liquid product, with small amount of yellow solid. The ^1H NMR showed that the liquid product was *o*-xylene (77%); δ_{H} 2.3 (6 H, s) and 7.1 (4 H, s), while the GCMS showed that the solid was *tetramethylbiphenyl* (7%); m/z 210. Repeat pyrolysis at 700 °C gave the same mixture of products.

3 Results and discussion

3.1 Benzyldiene chlorides

A range of substituted benzyldiene chlorides (dichloromethylarenes) **1a–k** were prepared from the corresponding benzaldehydes by treatment with either thionyl chloride or phosphorus pentachloride. In many cases these were characterised by NMR spectroscopy for the first time and the resulting data are given in the experimental section. Characteristic signals for the CHCl_2 function were observed at δ_{H} 6.6–7.2 (1H, s) and δ_{C} 64–70. As noted by previous authors, the compounds were not stable to prolonged storage and freshly prepared and distilled samples were used for the pyrolysis studies.

When the substituted benzyldiene halides were subjected to FVP over magnesium there was usually complete reaction at 600 °C and products accounting for between 56 and 92% overall yield were identified by a combination of NMR and GCMS methods (Scheme 1, Table 1). As expected from our previous studies on benzyl halides [2], the major product in most cases was that of dehalogenative coupling to give the stilbene mainly as the (*E*)-isomer **2** but accompanied by a smaller amount of the (*Z*)-isomer **3**. In favourable cases the pure (*E*)-stilbene could be obtained simply by recrystallisation of the solid at the furnace exit from ethanol and this occurred for **2a**, **2d** and **2h** while the previously unreported compound **2i** was obtained pure by preparative TLC. In all cases there were however varying amounts of other products, notably the reduction products: the bibenzyl **4** and the toluene **5**. As we noted previously [1], various pieces of evidence point to the involvement of surface-adsorbed organometallic species in these processes but the formation of apparent hydrogen atom abstraction products is consistent with the behaviour observed for benzylic halides [2]. A previous study on atmospheric pressure flow pyrolysis of **1a** under nitrogen at temperatures between 430 and 650 °C also gave 10–20% yields of **4** and **5** in addition to stilbene **2a** as the major product [26].



Scheme 1. Major products from FVP of benzylidene halides over magnesium

There were also some additional products specific to particular substitution patterns. Thus, for example the 2-methyl compound **1b** gave a 17% yield of benzocyclobutene as might be expected from insertion of a carbenoid into the adjacent methyl CH. The 3- and 4-methyl compounds had no such complication and gave higher yields of dimethylstilbenes.

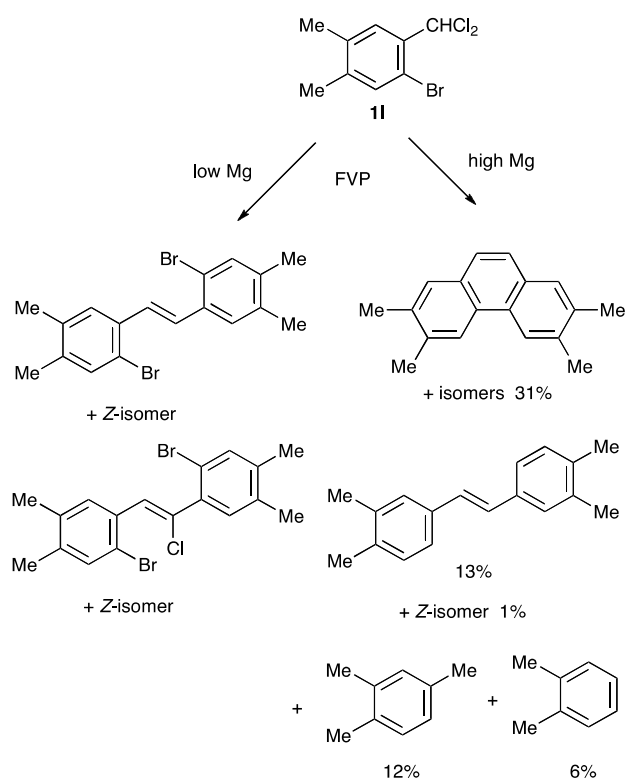
Table 1. Pyrolysis of benzylidene chlorides over magnesium at 600 °C

	R	g Mg / g 1	Press /Torr	Pyrolysis products yield (%)							Other products
				2	3	4	5	6	7	8	
1a	H	2.0	6.8×10^{-1}	42	7	20	12	<1	—	—	benzene (6%), styrene (1%), diphenylmethane (<1%)
1b	2-Me	1.8	7.0×10^{-1}	31	5	10	13	—	—	—	benzocyclobutene (17%), toluene (7%)
1c	3-Me	1.5	7.0×10^{-1}	42	6	12	11	—	—	—	toluene (5%), 3-methylstyrene (<1%)
1d	4-Me	2.4	7.0×10^{-1}	56	7	21	6	—	—	—	toluene (<1%), 4-methylstyrene (<1%)
1e	2-MeO	2.0	4.0×10^{-1}	—	—	—	—	—	—	—	toluene (61%), o-xylene (8%), benzocyclobutene (4%)
1f	4-MeO	1.3	7.8×10^{-1}	18 ^a	1 ^a	—	6 ^a	—	—	—	4-methoxystyrene (18%), ethylbenzene (7%), styrene (6%), anisole (4%), 4-methoxystilbene (3%)
1g	2-Cl	1.6	6.2×10^{-1}	8	—	—	2	6	41	8	toluene (2%), chlorobenzene (1%), 2-chlorobenzyl chloride(1%)
1g	2-Cl	4.0	6.4×10^{-1}	2 ^a	1 ^a	—	2 ^a	47	—	—	benzene (4%), 9,10-dihydrophenanthrene (1%)
1h	4-Cl	2.0	5.2×10^{-1}	16	7	<1	1	—	10	10	4-chlorostilbene (5%), benzene (2%), chlorobenzene (2%), toluene (2%)
1i	2-Cl-6-F	1.0	1.0×10^{-1}	48	10	—	2	—	4	—	<i>E</i> - and <i>Z</i> -tetrachlorodifluorostilbenes (5%), 2-chloro-6-fluorobenzyl chloride (7%)
1i	2-Cl-6-F ^b	3.0	1.8×10^{-1}	35	14	—	—	—	—	—	1,2-bis(2-chloro-6-fluorophenyl)ethyne (7%)
1j	2-Cl-4,5-OCH ₂ O	3.0	1.0×10^{-1}	10	2	—	—	5	—	—	
1k	2-Cl-5-NO ₂	3.0	1.5×10^{-1}	—	—	—	—	—	—	—	chlorophenanthrene (10%)

^a products formed with loss of R, i.e. **2a**, **3a** and **5a**^b at 650 °C

We believe these reactions proceed by a common mechanism illustrated for the case of **1e** in Scheme 3. The reactive centre created by magnesium removing the first chlorine atom interacts with the methoxy group with hydrogen atom abstraction and the resulting phenoxymethyl radical rearranges in a well-known process [29] to benzyloxy. Further dechlorination, deoxygenation and decarbonylation then occurs to give the observed products. The 4-methoxy compound **1f** also behaved in an unexpected way with predominant loss of the methoxy group and we conclude that methoxy substituents are in general not compatible with this method of gas-phase dehalogenative coupling.

Pyrolysis of 2-halo-substituted compounds with complete dehalogenation might be expected to lead to cyclisation giving phenanthrenes and indeed this was also the basis of our recent approach to benzodithiophenes [5]. Reaction of 2-chlorobenzylidene chloride **1g** initially led to incomplete dechlorination to give **7g** as the main product but, when the quantity of magnesium in the furnace was increased, phenanthrene **6** was formed in almost 50% yield. It appeared that this might be a useful method to construct specifically substituted phenanthrenes from monocyclic precursors in a single step. However when the 2-chloro-6-fluoro compound **1i** was examined it underwent only stilbene formation with no sign of further cyclisation. Interestingly when the amount of magnesium and pyrolysis temperature were increased the diarylalkyne appeared as a new minor product (7%). A further attempt to construct a functionalised phenanthrene was made using the compound **1j** but this gave only a low yield of the stilbene and the methylenedioxy group, like methoxy, is evidently not compatible with the conditions required for phenanthrene formation. The same was also the case for the nitro-containing compound **1k** which decomposed to give no useful products. A further attempt using a more carefully designed precursor did give more encouraging results (Scheme 4).



Scheme 4. Processes observed upon FVP of **11** over magnesium

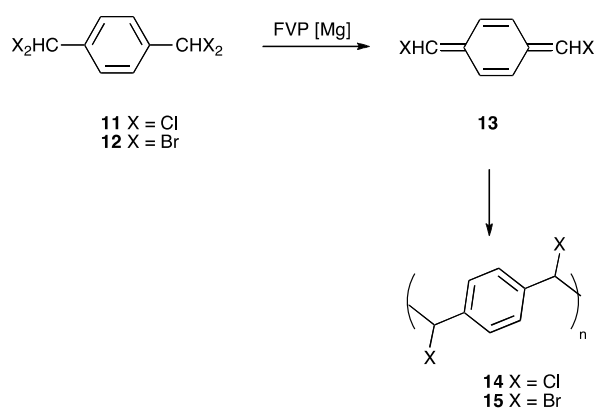
Compound **11** with two inert methyl groups and the more reactive *o*-bromine substituent was found to undergo stilbene formation on FVP through a smaller amount of magnesium, and when this was increased there was complete dehalogenation to give tetramethylphenanthrene as the main product. However even this was not without complication as the product was formed together with two tetramethylphenanthrene isomers (16, 12, 3%) which could not be separated or identified as they all had the expected molecular weight of 234.

We have shown in this section that FVP over magnesium is an effective method for coupling of substituted benzylidene chlorides **1** to give the corresponding (*E*)-stilbenes **2** which may be isolated in pure form by simple recrystallisation in some cases. However there are limitations with groups such as methoxy, methylenedioxy and nitro not being tolerated. For comparison, the coupling of **1a** to give **2** can be achieved using disilane reduction with palladium catalysis [30] but this also gives dichlorobibenzyl depending on the amount of silane used, and coupling of **1a**, **1f**, and **1h** occurs readily using a variety of tungsten carbonyl derivatives [31] giving mixtures of stilbenes **2** and **3**.

3.2 Tetrahaloxylenes

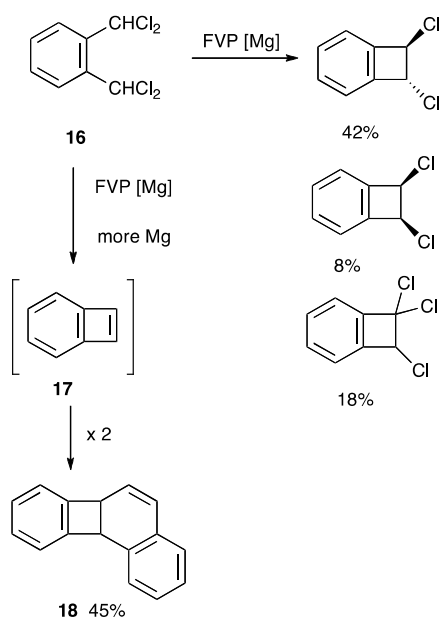
An obvious extension of the study was to examine compounds with two dihalomethyl groups on a benzene ring. In the case where these groups are *para*, halogenated *p*-xylylenes could be formed, and these are known to form a series of useful polymers [32]. To take the example of tetrafluoro-*p*-xylylene, a gas phase pyrolysis route was initially used industrially to form the stable dimer, octafluoro[2.2]paracyclophane, and this was a convenient precursor for vacuum pyrolytic regeneration of the *p*-xylylene and direct deposition of a highly crystalline "parylene" polymer film [33]. Later a more convenient route to the cyclophane was developed [34] making the polymer production commercially viable, and shortly thereafter the xylylene was isolated in a matrix and characterised spectroscopically [35].

The tetrachloro and tetrabromo-*p*-xylenes **11** and **12** were readily formed from terephthalaldehyde and when these were subjected to FVP over magnesium uniform colourless films of polymers were deposited in the cold trap with compositions from elemental analysis and solid state NMR corresponding to the halogenated polymers **14** and **15** expected from the monomers **13** (Scheme 5). Thermogravimetric analysis showed these to be relatively unstable upon heating as expected from the presence of adjacent CHX groups.



Scheme 5. Pyrolysis of tetrahalo-*p*-xylylenes over magnesium to form polymers

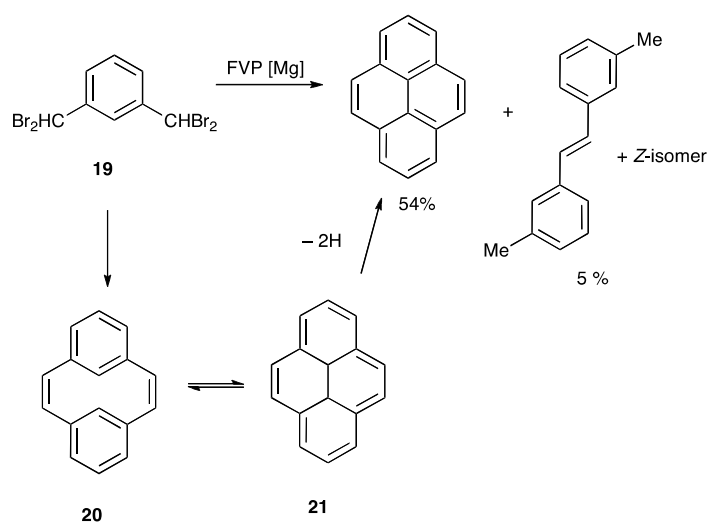
The pyrolysis of tetrabromo-*o*-xylene over magnesium was the method used to generate benzocyclobutadiene allowing it to be detected by photoelectron spectroscopy for the first time [36] and represents one of the earliest literature uses of this method. When we subjected the corresponding tetrachloro-*o*-xylene **16** to our conditions the outcome was found to depend on the amount of magnesium used. With a smaller amount of magnesium there was only partial dechlorination with some loss of HCl to form a mixture of di- and trichloro benzocyclobutenes identified by comparison with literature data [21,22] (Scheme 6). When the amount of magnesium



Scheme 6. Pyrolysis of tetrachloro-*o*-xylene over magnesium

was increased complete dehalogenation was observed and the main product isolated was the known dimer of benzocyclobutadiene **17**, the tetracyclic hydrocarbon **18** [23].

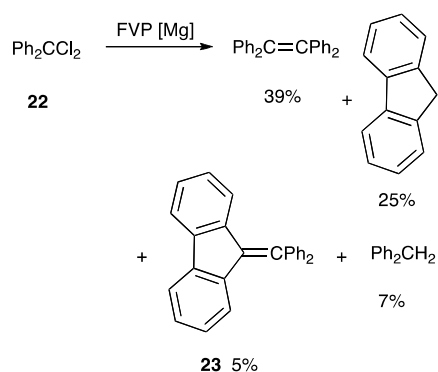
Finally in this section, we examined the tetrabromo-*m*-xylene **19** and found that it reacted efficiently over magnesium to give pyrene as the main product together with a little 3,3'-dimethylstilbene (Scheme 7). The likely mechanism involves dehalogenative coupling to form the cyclophane **20** which is known [37,38] to undergo electrocyclisation to dihydropyrene **21** followed by ready aromatisation.



Scheme 7. Pyrolysis of tetrabromo-*m*-xylene over magnesium to give pyrene

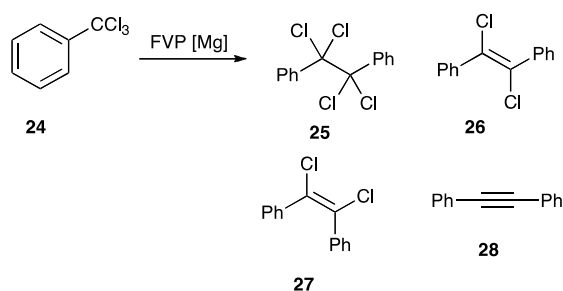
3.3 Dichlorodiphenylmethane and mono- and bis(trihalomethyl)benzenes

Dehalogenative coupling of dichlorodiphenylmethane **22** to give tetraphenylethene has been reported using a variety of agents including metallic zinc [39], finely divided nickel [40], and either $W(CO)_6$ or $WCl_6 / LiAlH_4$ [31]. Subjecting **22** to our conditions did give tetraphenylethene as the major product but this was accompanied by a 25% yield of fluorene, 7% of diphenylmethane and 5% of 9-diphenylmethylenefluorene **23** (Scheme 8).



Scheme 8. Pyrolysis of dichlorodiphenylmethane over magnesium

When benzotrichloride **24** was subjected to FVP over magnesium the products formed were tetrachlorobiphenyl **25**, the E and Z isomers of dichlorostilbene **26** and **27** and diphenylacetylene **28** (Scheme 9). However the yields were found to depend on the pressure and thus contact time as shown in Table 2.



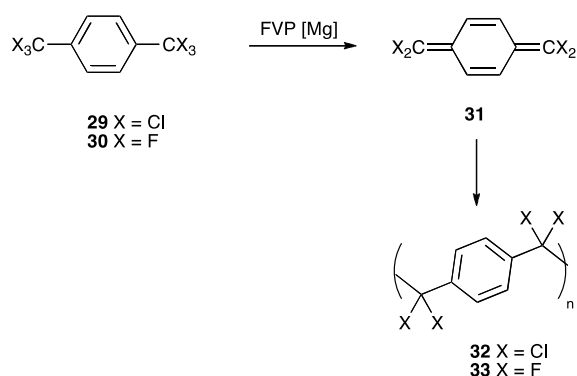
Scheme 9. Pyrolysis of benzotrichloride over magnesium

Table 2. Dependence of product composition on pressure for **24**

pressure /Torr	yield/%			
	25	26	27	28
0.2	22	23	19	12
1.0	8	21	20	30

It is clear that longer contact time leads to more extensive dehalogenation and increased formation of the alkyne **28** at the expense of tetrachloride **25**. Previous studies on dehalogenative coupling of **24** include the use of both zinc [39] and finely divided nickel [40] to give exclusively **26/27** with the *E/Z* ratio in the latter case being 74:26. Using iron powder in water, the coupling was shown to proceed stepwise by initial formation of **25** which was then further reduced to **26** [41]. The corresponding reaction of benzotrifluoride proved to be much more difficult and under comparable conditions the starting material came through the furnace mostly unchanged, but accompanied by a small proportion of products corresponding to those from **24**.

Again we saw the opportunity to generate halogenated *p*-xylylenes and thus the corresponding polymers by FVP of 1,4-bis(trihalomethyl)benzenes.

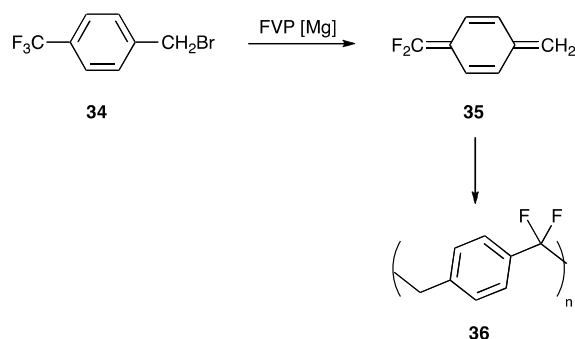


Scheme 10. Pyrolysis of 1,4-bis(trihalomethyl)benzenes over magnesium

When either hexachloro-*p*-xylene **29** or hexafluoro-*p*-xylene **30** were subjected to FVP over magnesium the main product was a transparent polymeric film

deposited in the cold trap. Elemental analysis, and in the former case solid state NMR, was consistent with these being poly(tetrachloro-*p*-xylylene) **32** and poly(tetrafluoro-*p*-xylylene) **33** formed by polymerisation of the relevant tetrahalo-*p*-xylylenes **31** (Scheme 10). The molecular weight was estimated in the case of **32** by end group analysis and corresponded approximately to a decamer. As documented in the literature for these two polymers, they showed exceptional thermal stability with **32** being stable up to over 300 °C [32] and the fluorinated polymer **33** being stable up to nearly 600 °C [35].

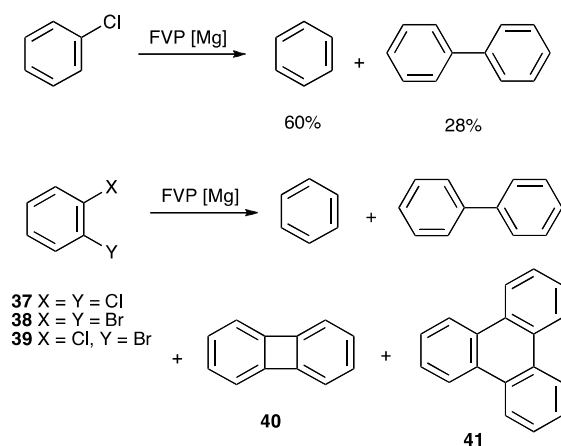
A similar method gave access to the unsymmetrical difluoro-*p*-xylylene **35** and thus the polymer **36** (Scheme 11). The required starting material **34** gave some non-polymeric products in addition to being partly unchanged such as 4,4'-bis(trifluoromethyl)bibenzyl and *p*-trifluoromethyltoluene. However a 12% yield of polymer was formed which gave elemental analysis and solid state NMR results consistent with the structure **36**. This was notably less thermally stable than either **32** or **33**.



Scheme 11. Pyrolysis of 4-bromomethylbenzotrifluoride over magnesium

3.4 Halobenzenes

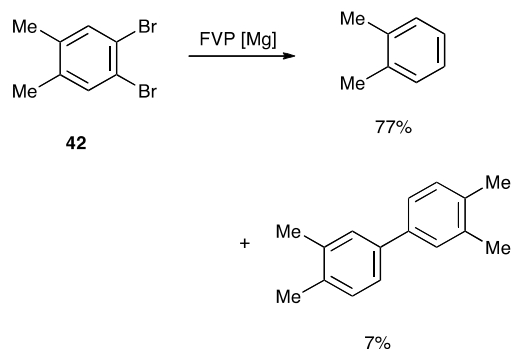
The final class of organic halides investigated was the halobenzenes. Chlorobenzene reacted efficiently upon FVP over magnesium at 600 °C to give a mixture of benzene and biphenyl (Scheme 12). These products can be explained by



Scheme 12. Pyrolysis of mono and *o*-dihalobenzenes over magnesium

invoking either a phenyl radical intermediate or a phenylmagnesium species which can dimerise or pick up hydrogen. A similar mechanism applied to *o*-dihalobenzenes would seem to have the possibility of generating benzyne. Indeed when either *o*-dichlorobenzene **37** or *o*-dibromobenzene **38** was submitted to FVP over magnesium at 600 °C there was some unchanged starting material together with benzene and biphenyl but these were now accompanied by significant yields of both biphenylene **40** and triphenylene **41** (Scheme 12). By increasing the furnace temperature to 700 °C the unreacted starting material was avoided and the remaining products were found to be distributed in the cold trap according to volatility, with benzene as a liquid in the coldest part, biphenyl and biphenylene as a solid in the middle, and triphenylene in almost pure form nearest the furnace exit. Using the unsymmetrical precursor 1-bromo-2-chlorobenzene **39** still gave some starting material at 600 °C but the yield of triphenylene was improved so that from **37** or **38** at 700 °C or **39** at 600 °C an isolated yield of 11-13% of triphenylene could be consistently obtained. Biphenylene **40**, first isolated in 1941 [42], is the normal product from gas phase generation of benzyne but it was never formed here in more than 1% yield. In contrast, solution reaction of *o*-metallated halobenzenes is known to give a good yield of triphenylene in a process where benzyne reacts with its precursor leading to formation of the apparent trimer. The high selectivity toward triphenylene as opposed to biphenylene observed here is strong evidence that free benzyne in the gas phase is unlikely to be involved and the formation of triphenylene more likely proceeds stepwise on the metal surface.

We sought to apply the method to the construction of a substituted triphenylene and prepared 4,5-dibromo-*o*-xylene **42**. When this was subjected to the normal conditions however, the products were only *o*-xylene and 3,3',4,4'-tetramethylbiphenyl (Scheme 13). We conclude that the presence of methyl groups acts as a source of hydrogen and prevents the formation of the triphenylene in any significant amount.



Scheme 13. Pyrolysis of 4,5-dibromo-*o*-xylene over magnesium

4 Conclusion

While gas-phase dehalogenative coupling over magnesium has proved to be a viable synthetic method in some cases, various limitations are also apparent. Substituted benzyldene chlorides **1**, readily formed from benzaldehydes, undergo selective reaction to form the (*E*)-stilbenes **2** which can be isolated in pure form in some cases. The method is not compatible with the presence of groups such as methoxy, methylenedioxy or nitro. Both tetrahalo and hexahalo-*p*-xylenes act as precursors for gas-phase generation of halogenated *p*-xylylenes, useful for direct

deposition of high performance polymers **14**, **15**, **32**, **33** and **36**. Tetrachloro-*o*-xylene reacts to afford benzocyclobutadiene isolated as its dimer **18** and tetrabromo-*m*-xylene similarly forms pyrene via the cyclophane **20**. Reaction of the readily available 1,2-dihalobenzenes provides a viable method for synthesis of triphenylene **41** with the negligible formation of biphenylene ruling out the involvement of free gas-phase benzyne.

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Highlights

- FVP over magnesium couples benzylidene chlorides to give mainly stilbenes
- *Ortho*-methoxybenzylidene chlorides unexpectedly give hydrocarbon products
- Halogenated poly(*p*-xylenes) are deposited direct from pyrolysis of halogenated *p*-xylenes
- Dichlorodiphenylmethane gives 9-(diphenylmethylene)fluorene
- Triphenylene is formed in moderate yield from 1,2-dihalobenzenes
- The method offers a convenient one-step solvent-free alternative to catalytic procedures

Graphical Abstract

